Time-Resolved Small-Angle X-ray Scattering Study of the Kinetics of Disorder-Order Transition in a Triblock Copolymer in a Selective Solvent for the Middle Block

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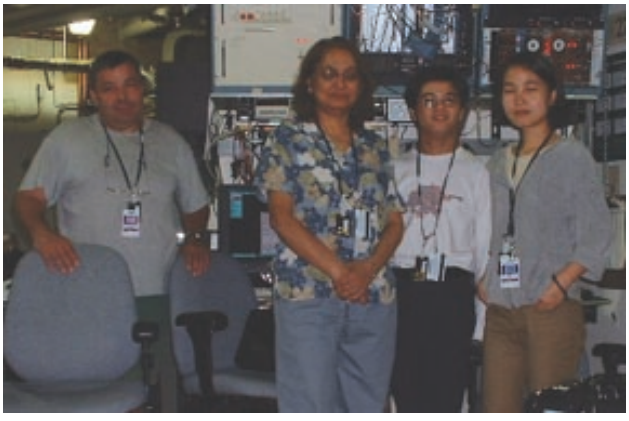
Solutions of block copolymers in solvents that selectively dissolve one of the component polymers form micelles with the insoluble component in the cores. These complex fluid or gel states exhibit a rich phase diagram with many different ordered structures. Understanding the phase behavior and kinetics of these materials is of considerable importance to controlling their properties. We reported the first time-resolved small angle x-ray scattering (SAXS) study on the kinetics of the formation of a bcc ordered state from a disordered micellar fluid in solutions of Kraton, a commercial triblock copolymer. Our studies reveal a two-stage process that shows significant change of the micelle's size at the onset of ordering.

Solutions of multi-block copolymers exhibit rich phase diagrams and novel morphologies, and can form clusters, networks, and gels. These properties determine their numerous applications, such as detergents, adhesives, elastomers, bio-mimetic vesicles, and templates for nanomaterials. The phase behavior and properties of these materials can be tuned by varying the number of component polymers and blocks, the chemical composition and length of the blocks, and the blocks' interactions with solvents. For example, an ABA triblock copolymer solution in a solvent that is good for the outer (A) block forms isolated micelles with cores containing the B block. On the other hand, in a solvent that is good for the middle B block, loops or bridges will be formed and the middle block can tether two adjoining micelles, eventually forming a network. The micelles, which can be either spherical or cylindrical, either exist as a complex fluid or form ordered structures, such as cubic or hexagonal. Our focus is to understand the kinetics of the phase transitions between the different disordered and ordered states of the micellar phases of these solutions. Since the micellar cores are on nanometer-length scales and the phase transitions occur on the time scale of minutes, synchrotron based time-resolved small angle x-ray scattering (SAXS) is an ideal tool for examining their structure and kinetics.

A few SAXS studies of the kinetics of order-order and order-disorder transitions in melts of block copolymers have been reported. To the best of our knowledge, our recent publication is the first temperature jump study of isothermally evolving kinetics in solutions of triblocks. We examined the disorder-order transition kinetics of a styrene (S) ethylene-co-butylene (EB) triblock



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copolymer, SEBS, in mineral oil, which preferentially dissolves the middle EB block. This commercial thermoplastic elastomer from Shell, known as Kraton®, is used in footwear, adhesive sealants and coatings, roofing, and packaging. Using the high flux monochromator at beamline X27C and a one-dimensional wire detector, we were able to measure the scattered intensity I(q) as a function of the wavenumber, q, with a time resolution of 10 seconds over the q-range 0.01 to 0.3 $Å^{-1}$, and thus follow the kinetics of the micellar fluid's ordering onto a bcc lattice. The transition was typically followed either by ramping the temperature over a wide range (**Figure 1**) or by rapidly quenching the sample temperature into the ordered phase (**Figure 2**). The temperature ramp experiment identifies the phase transition temperature, while the temperature quench experiment provides the isothermal kinetics. A model based on interacting hard spheres was used to analyze the data and provide detailed information about the time evolution of the micellar structural parameters during the ordering process. For example, the results showed that the core radius decreased sharply at the onset of the ordering process (**Figure 3a**). The kinetics exhibits two stages corresponding to temperature equilibration and supercooling of the micellar fluid, followed by the nucleation and growth of the ordered state **(Figure 3b**). The induction-time for the onset of the second stage shows a minimum around the glass transition temperature of the polystyrene cores.

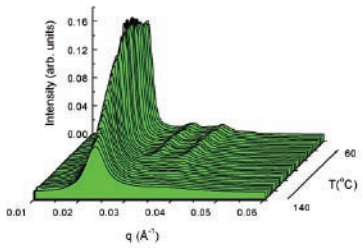

Figure 1. The development of Bragg peaks in the scattering intensity *I(q)* versus *q* during a cooling ramp from 140 to 60°C show a transition from a disordered micellar fluid at high temperatures to a bcc structure below about 120°C. The primary peak in the high-temperature data is due to the interacting micellar cores in the fluid phase.

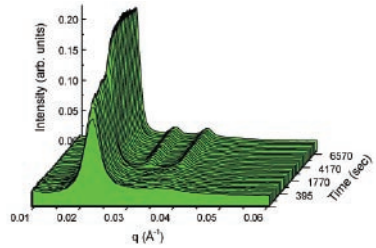

Figure 2. The time evolution of the scattering intensity *I(q)* versus *q* following a rapid jump from 140°C to 96°C shows the isothermal growth kinetics of the ordered bcc structure at the final temperature of 96°C. The delayed appearance of the higher Bragg peaks indicates a two-stage process. Note that the temperature of the sample equilibrates within 60 seconds following the jump.

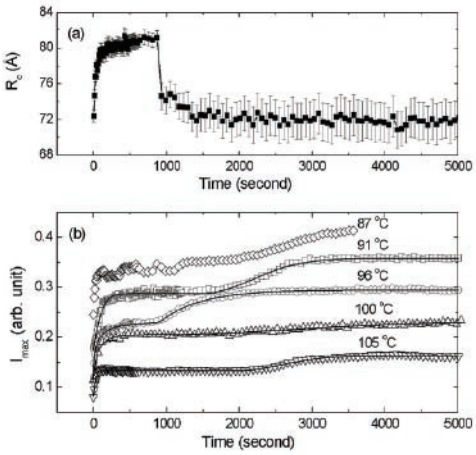

Figure 3. (a) The time evolution of the core radius R_c of the micelles following the quench from 140 °C to 96 °C shows a sudden decrease in the size of the micelle at the onset of ordering, at around 1000 seconds. (b) Temporal evolution of the primary peak's intensity following quenches from 140°C to different final temperatures, as indicated on the graph. The data reveal two stages in the ordering process. Note that the data are offset by different constants for visual clarity.